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NSG - (CT) - 140

Improved Preparation of 9-Octadecenes

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 J. Am. Oil Chemists' Soc. 43, 431-432 (1966)

(HC) \$1.00
 (MF) .50

Abstract

cis- and trans-9-Octadecenes have been obtained in about 55-60% yield on a preparative scale by an improved procedure from commercially pure oleyl alcohol (90-95%) and elaidyl alcohol, respectively, by conversion to the tosylates followed by reduction with lithium aluminum hydride (LAH). The improvement consists in using saturated sodium chloride solution to coagulate the slimy, intractable, insoluble salts obtained after the LAH reduction and destruction of excess LAH with water, prior to ether extraction of the crude hydrocarbons. Total time required for the preparation is about three days.

cis- and trans-9-Octadecene are valuable model compounds for use in the development and study of new reactions of fats and their derivatives. The introduction of functional groups into these relatively simple, uncomplicated molecules can be readily followed by a variety of physical and chemical methods. Since the solubility and volatility characteristics of these long chain unsaturated hydrocarbons are similar to those of fatty acid derivatives, it is preferable to use them as model compounds rather than analogous shorter chain olefins, such as trans-3-hexene and 2-octene.

The preparation of cis- and trans-9-octadecene from methyl oleate and elaidate (or oleyl and elaidyl alcohol), respectively, is described in the literature (1), but the procedures are inadequately described or the scale of the preparation is too small to be generally useful. Most important, however,

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is that the literature procedures, at least in our hands, are not readily duplicated and leave much to be desired in the way of yield and purity of final products.

The usual procedure for obtaining the 9-octadecenes is: (a) reduction of methyl oleate or elaidate with lithium aluminum hydride (LAH) to the corresponding alcohols, (b) conversion of the alcohols to the toluenesulfonate esters (tosylates), (c) reduction of the tosylates with LAH to the unsaturated hydrocarbons, and (d) fractional distillation of the crude hydrocarbons. Flowsheet 1 summarizes the procedure.

Although the yields in each step are high, the major problem in the reaction sequence shown in Flowsheet 1 is the separation of the crude unsaturated hydrocarbons from the tosylate reduction mixture. This mixture, after destruction of excess LAH with water, also contains slimy, intractable inorganic salts and salts of toluenethiol, the other reduction product of the tosylate. Acidification of this reduction mixture dissolves the insoluble salts and permits facile extraction of the hydrocarbons but toluenethiol is also formed and this compound is a good cis-trans isomerization catalyst, besides having an objectionable odor. The presence of toluenethiol in the hydrocarbons during the final workup and especially during the fractional distillation should be scrupulously avoided. Alternatively, the slimy salts can be separated by filtration but the experience is very discouraging, especially on a preparative scale (100-200g.)

We have found that the final reaction mixture can be maintained on the alkaline side and the hydrocarbons readily extracted from the lithium and/or aluminum salts by adding saturated sodium chloride solution. This coagulates the inorganics and permits the extraction with ether to proceed readily. The ether solution is dried and, after evaporation of the ether, the crude hydrocarbons are distilled.

In the work described in this Note, we started with a good commercial grade of oleyl alcohol containing about 90-95% octadecenols, of which about one-fourth had the trans- configuration (Fig. 1). This starting material was selected because of its low price and availability and also because we wished to test and check the procedure on a fairly large scale with both undergra-

Methyl oleate (or elaidate)



LAH (ether or tetrahydrofuran)

Oleyl alcohol (or elaidyl alcohol)



Toluenesulfonyl chloride-pyridine

Oleyl tosylate (or elaidyl tosylate)



LAH (tetrahydrofuran)

cis-9-Octadecene (trans-9-Octadecene)

FLWSHEET 1

and graduate students. We did not wish to commit ourselves to too large an expenditure of time and money to obtain 100% cis-9-octadecenol.

The most important question to be answered was whether the cis/trans ratio is altered by the procedure. The octadecenes we obtained from commercial oleyl alcohol contained about 15-20% of trans-isomers (Fig.2), showing apparently that no alteration in the double bond system had occurred. Overall yield of distilled 9-octadecenes, b.p. 133°/0.5 mm., was 55% based on the oleyl alcohol starting material. GLC analysis on a 10'x1/4" 10% butanediol succinate column on Anakron ABS showed that the hydrocarbon product contained >98% of C-18. Portions of three consecutive working days were sufficient for the preparation.

The procedure was repeated on a larger scale with the more readily accessible pure trans-9-octadecenol (elaidyl alcohol) (Fig. 3) as the starting material. trans-9-Octadecene, b.p. 138-141°/0.3 mm. and m.p. 12-13°, was obtained (Fig. 4) in about 60% yield from the alcohol. The melting point of the trans-9-octadecene we obtained was significantly higher than the literature value of 5° (1).

Experimental

Starting Materials: Adol 90, obtained from the Archer-Daniels-Midland Co., was used for the preparation of 9-octadecenes. It contained about 20% of trans-isomers (Fig. 1). Elaidyl alcohol (Fig. 3), m.p. 35.3-36.0°, was prepared from pure oleyl alcohol by short-time selenium isomerization at 225° (2). LAH was obtained from Metal Hydrides, Inc. All solvents were of highest quality; they were dried and distilled before use. p-Toluene-sulfonyl chloride, m.p. 63-5°, was Eastman White Label Grade.

Infrared Spectra: A Perkin-Elmer Infracord Spectrophotometer Model 137 B with 0.103 mm. matched cells was used. Approximately 4% solutions in carbon tetrachloride were examined. Infrared spectra are shown in Figs. 1-4.

Procedure: 9-Octadecenes. In a 1 liter, three-neck flask equipped with a stirrer and thermometer, commercial oleyl alcohol (100 g.; 0.37 mole) was dissolved in 200 ml. of dry pyridine. The stirred solution was cooled to 10-15° in an ice bath and p-toluenesulfonyl chloride (96 g.; 0.5 mole) was

added in 3-5 equal portions over a 30-45 minute period. The solution was stirred for 2-3 hours and then placed in a refrigerator overnight.

The solid-liquid slush from the refrigerator was poured into a separatory funnel and extracted with 4 x 200 ml. of petroleum ether using a minimum volume of water (10-20 ml.) or, if necessary, saturated sodium chloride solutions to separate the layers. The combined petroleum ether extracts were washed with 10 x 250 ml. of water, dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent under vacuum in a rotary evaporator yielded 137 g. (87% yield) of tosylates as a pale yellow oil.

The tosylates, dissolved in 300-500 ml. of anhydrous tetrahydrofuran (THF), were added dropwise over a 30-45 minute period to a stirred refluxing mixture of 500 ml. of THF and LAH (15 g.; 0.4 mole) in a three-neck flask equipped with an efficient condenser to which a calcium chloride drying tube was attached. When addition was complete, stirring and refluxing were continued for an additional 30-45 minutes.

The heater was then replaced by an ice bath and the reaction mixture was cooled to room temperature. With caution, 10 ml. of a 10% aqueous solution of sodium hydroxide was added dropwise to destroy the excess LAH. In this step, considerable heat is evolved and an efficient ice bath should be used. To coagulate the insoluble salts, 100-200 ml. of a saturated sodium chloride solution was added and the mixture was stored overnight in a refrigerator.

The solid-liquid mixture was extracted in portions with 3 x 100 ml. volumes of ether and the lower aqueous phase containing salts was discarded. (Occasionally saturated sodium chloride solution had to be added to effect a clean separation of layers). The ether extracts were washed with water until free of salt, dried over anhydrous magnesium sulfate and filtered. Evaporation of the ether in a rotary evaporator gave 68 g. (84% yield based on tosylate) of crude hydrocarbons as a yellow oil. Distillation through a 3' x 1" heated Vigreux column yielded 55 g. (59% yield based on oleyl alcohol) of colorless 9-octadecenes, b.p. 133°/0.5 mm. The heart cut had n_D^{26} 1.4464 [lit. n_D^{25} 1.4450 (1)] and contained about 17% of trans isomers

(Fig. 2) (3). GLC analysis through a 10' x 1/4" 10% butanediol succinate column of Anakron ABS indicated >98% C-18.

trans-9-Octadecene. In similar fashion, elaidyl alcohol (200 g.; 0.75 mole) and p-toluenesulfonyl chloride (160 g.; 0.83 mole) in 500 ml. of dry pyridine yielded 235 g. (75%) of elaidyl tosylate which on LAH reduction in a total of 1700 ml of refluxing THF for two hours followed by fractional distillation yielded 105 g. (55% yield based on elaidyl alcohol) of trans-9-octadecene, b.p. 138-141°/0.3 mm. and m.p. 12-13° [lit. 5° (1)]. It was a colorless liquid the infrared spectrum of which is shown in Fig. 4.

Acknowledgment: The authors are grateful to Kenneth Craig and Armin Wolle, undergraduates in the Advanced Organic Preparations course at Temple University, for checking the procedures. This investigation was supported in part by Public Health Service Research Grants No. CA-07803 and CA-07174. Martin E. Dyen was supported partially under a Training Grant Award 520-831-00 from NASA.

Legend For Figures

- Fig. 1: Infrared Absorption Spectrum Of Commercial Oleyl Alcohol Starting Material.
- Fig. 2: Infrared Absorption Spectrum Of 9-Octadecenes Obtained From Commercial Oleyl Alcohol.
- Fig. 3: Infrared Absorption Spectrum Of trans-9-Octadecenol (Elaidyl Alcohol).
- Fig. 4: Infrared Absorption Spectrum Of trans-9-Octadecene.

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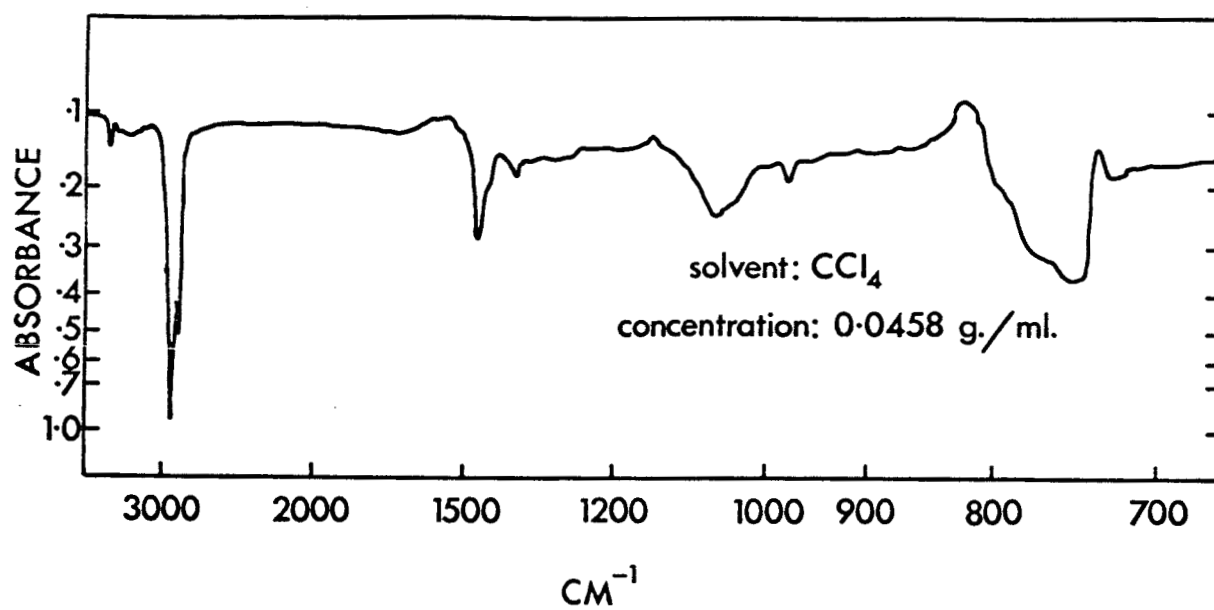


Figure 1

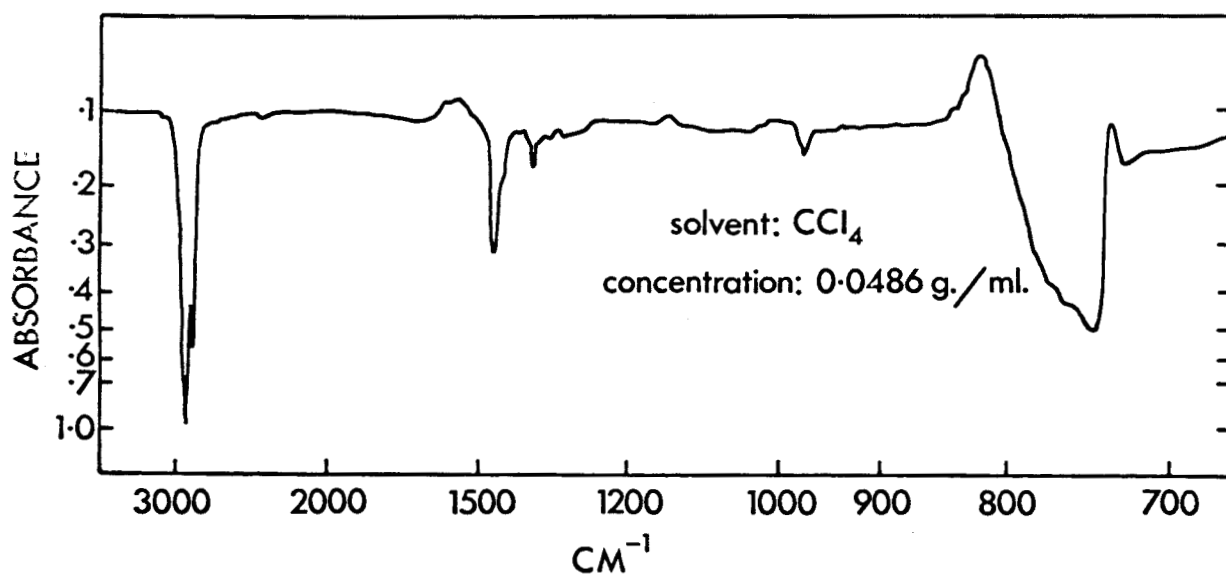


Figure 2

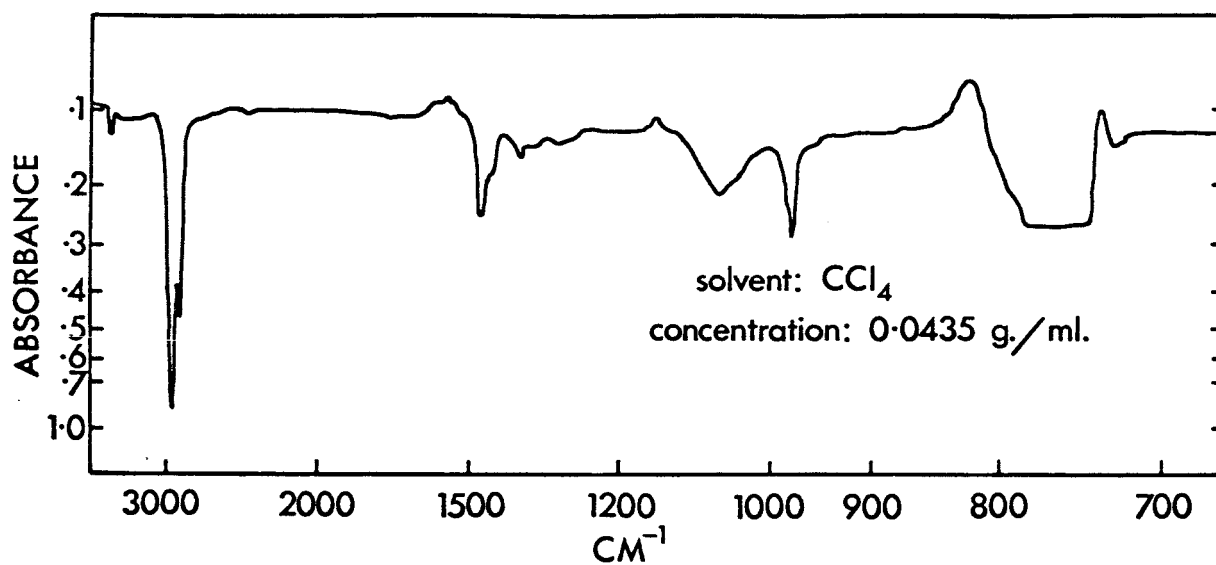


Figure 3

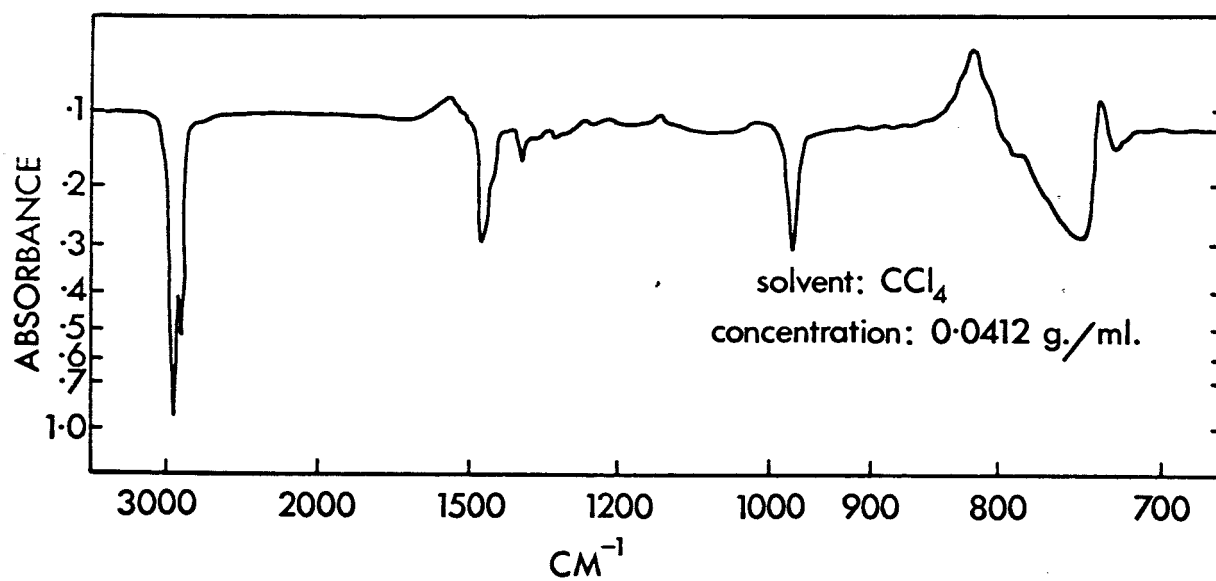


Figure 4